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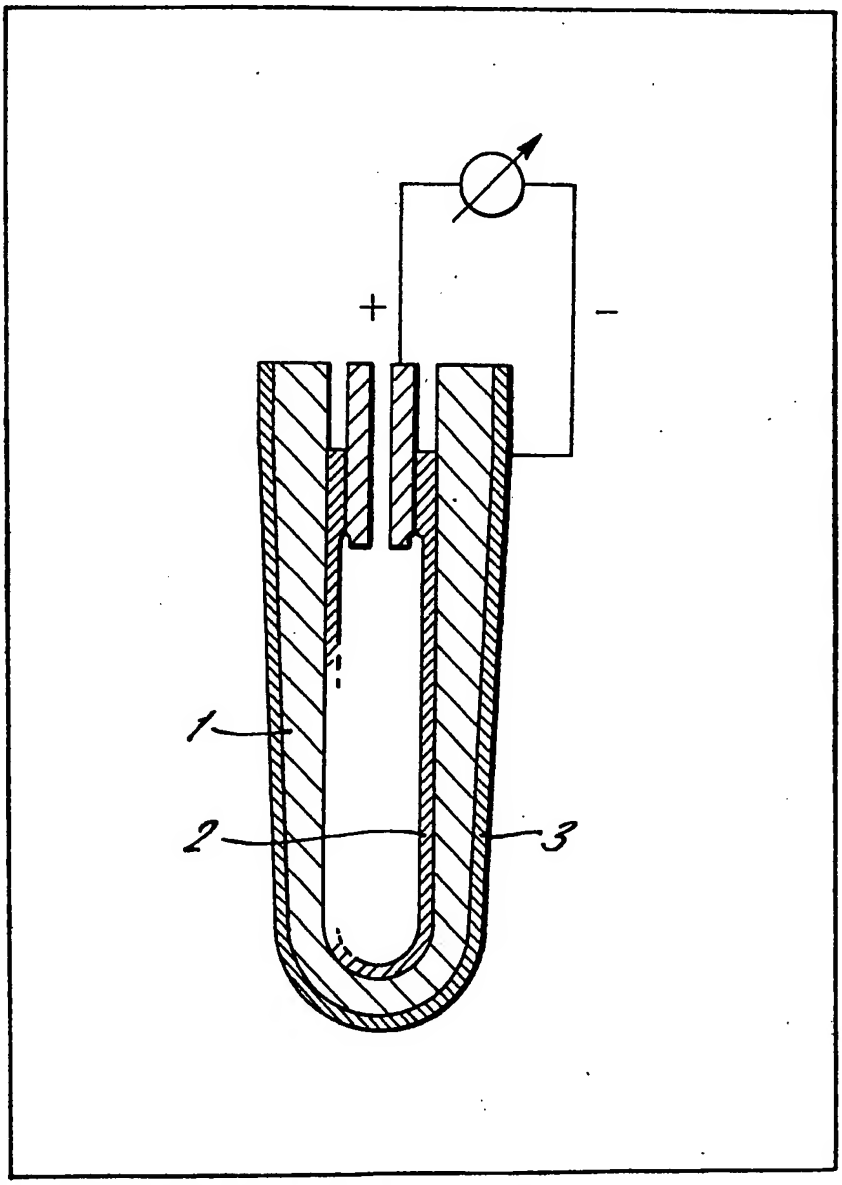
(54) Solid state oxygen sensor

(57) A solid state oxygen sensor for measuring partial pressures of oxygen, which sensor is constituted by an electrolyte cell (1) whose oxygen-sensitive measuring electrodes (3) is one or more non-stoichiometric oxides, the electrolyte being a solid state ceramic.

The oxides may have mixed conductivity, both ionic and electronic and may be either non stoichiometric oxides alone or mixtures of such oxides.



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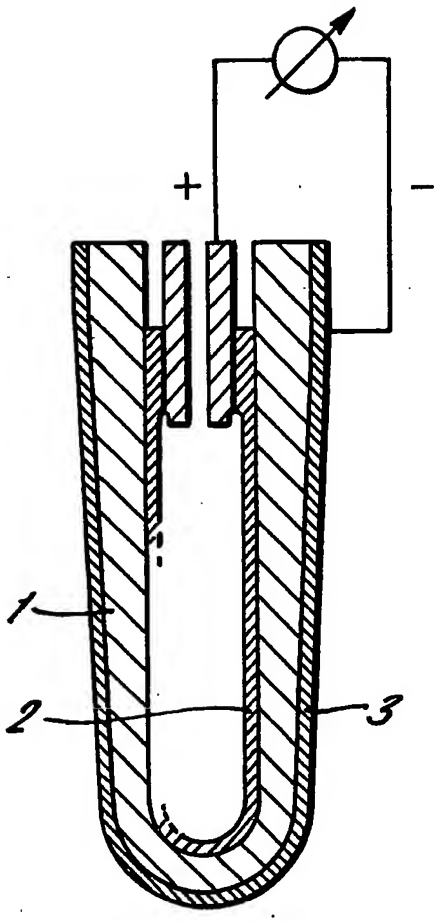
The drawing originally filed was informal and the print here reproduced is taken from a later filed formal copy.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SPECIFICATION

Solid state oxygen sensor

The present invention relates to solid state electrochemical devices for measuring oxygen activity, which devices include a solid oxide electrolyte and oxides as the oxygen sensitive electrodic material.

Electrochemical cells are known in the art for the measurement of the partial pressure of oxygen, which are constituted by a solid oxide electrolyte having as its electrodes unoxidisable electronic conductors, for example consisting of one of the noble metals, particularly: Pt.

The solid electrolyte is a ceramic oxide or a vitreous phase with pure ionic conduction, for example, a solid solution of oxides defective in oxygen ions.

Said cells, hereinafter called "oxygen sensors" have various drawbacks principally due to the metallic electrodic material (Pt), which considerably limits their possibilities of use.

In fact, the oxygen partial pressures measured are inferior to real values, when in the gas mixtures to be analysed there are present traces of oxidisable substances, such as H_2, CO, SO_2 and hydrocarbons.

When measuring the oxygen activity in CO/CO_2 mixtures, one observes a good precision in determining the ratio of the two gases, but the response times are very high for fast changes in the gas mixture composition.

When SO_x (x=2 or 3) is present in the gases to be analysed, the response times are very high.

Many metals may poison said electrode material (Pt) and the utilisation of the oxygen sensor in the control of the reducing atmosphere in metal-lurgical application, sometimes, is very critical or impossible.

Particularly, the electrode material (Pt) is easily poisoned by Pb; for this reason the use of such a device for the control of exhaust emission from an engine fed with gasoline containing Pb-organometallic compounds is excluded.

For obviating the said defects and for producing an electrochemical solid state oxygen sensor capable of being used in a wider range of application, we propose, according to the present invention, a new solid state electrochemical device in which the electrodic material (generally an unoxidisable electronic conductor, such as a noble metal) is constituted by oxide materials with mixed ionic and electronic electrical conductivity.

Such materials are either non-stoichiometric oxides (PrO_{2-x}, TbO_{2-x} or mixtures of said oxides e.g.: $TbO_{2-x}+CeO_{2-x}$; $PrO_{2-x}+CeO_{2-x}$) or mixed oxides ($LaCrO_3$; $La_{1-x}Sr_xCrO_3$ and so on).

The present invention will now be described, by way of example, with reference to the accompanying drawing, which shows the embodiment of the sensor of the present invention taken in longitudinal cross-section.

In Figure 1 is shown a container 1 made of a ceramic material, constituting the solid electrolyte, with its internal wall 2 and/or external wall 3 being in contact with an oxide (oxygen sensitive electrode).

The internal reference compartment uses a chemical system consisting of either a gaseous mixture (e.g. pure O_2, air, an oxygen gas mixture, CO/CO_2 or H_2/H_2O mixtures) or a metal-oxide mixture, e.g.: Ni, NiO, Fe-FeO etc. for fixing a known oxygen partial pressure.

The internal reference compartment uses as its oxygen sensitive electrode either a noble metal or an oxide.

The external electrode is placed in the gas atmosphere to be analysed and its oxygen sensitive material is either an oxide or a mixture of oxides.

Under operational conditions, an e.m.f. is observed between the said electrodes 2 and 3 as schematized in Fig. 1. It is the value of this e.m.f. which gives the measure of the oxygen activity.

The device according to the present invention may be industrially employed in the following fields:

a) atmosphere control in the thermal treating of metals;

b) combustion control in steam generators, furnaces and boilers;

c) control of the exhaust gases from internal combustion engines; and

d) to improve the combustible economy and antipollution device.

Claims

1. A solid state oxygen sensor for measuring partial pressures of oxygen, which sensor is constituted by an electrolyte cell whose oxygen-sensitive electrodes are non-stoichiometric oxides, the electrolyte being a solid state ceramic.

2. A solid state oxygen sensor as claimed in claim 1 wherein the oxygen-sensitive electrodes are oxides with mixed conductivity, ionic and electronic.

3. A solid state oxygen sensor as claimed in claim 1 wherein the oxygen-sensitive electrodes are oxides containing the potential poisoning metal present in the gas atmosphere to be analysed.

4. A solid state oxygen sensor as claimed in claim 1 wherein the oxygen sensitive electrodes are mixed oxides containing two or more cations.

5. A solid state oxygen sensor as claimed in claim 1 wherein the oxygen sensitive electrodes are mixtures of oxides.

6. A solid state oxygen sensor as claimed in claim 1 wherein the cell is formed by a solid state ceramic container having one wall in contact with the oxides which constitute the oxygen-sensitive electrode.

7. A solid state oxygen sensor as claimed in claim 1 wherein the cell is formed by a solid state ceramic container having both walls in contact with the oxides constituting the oxygen-sensitive electrodes.

8. A solid state oxygen sensor as claimed in claims 1 to 5 wherein the cell has one wall in

contact with mixtures of the oxides constituting the oxygen-sensitive electrode.

9. A solid state oxygen sensor as claimed in any one of claims 1 to 5 wherein the cell has both walls in contact with mixtures of the oxides.

10. A solid state oxygen sensor as claimed in any one of claims 1 to 4 wherein the outer wall surfaec of the cell is coated with $Pr\ O_{2-x}$.

11. A solid state oxygen sensor as claimed in any one of claims 1 to 4 wherein the outer wall surface of the cell is coated with TbO_{2-x}.

12. A solid state oxygen sensor as claimed in any one of claims 1, 2 or 6 wherein the outer surface is coated with TbO_{2-x} + and/or $PrO_{2-x}+CeO_{2-x}$.

13. A solid state oxygen sensor as claimed in any one of claims 1, 2 or 4 wherein the outer surface is coated with oxides of lantanides.

14. A solid state oxygen sensor as claimed in any one of claims 1, 2 or 6 wherein the outer surface is coated with mixed oxides of lantanides and/or transition metals.

15. A solid state oxygen sensor as claimed in any one of claims 1, 2 or 6 wherein the outer surface of the solid electrolyte is coated with mixed oxides of at least one of lantanides, transition and alkaline metals.

16. A solid state oxygen sensor as claimed in any one of claims 1, 2 or 6 wherein the outer surface is coated with mixed oxides of at least one of lantanides, transition and alkaline earth metals.

17. A solid state oxygen sensor as claimed in any one of claims 1, 2 or 6 wherein the outer surface of the solid electrolyte is coated with mixed oxides of at least one of lantanides, transition, alkaline earth metals.

18. A solid state oxygen sensor as claimed in any one of claims 1, 2 or 6 wherein the cell is formed by a solid state ceramic container having one wall in contact with a noble metal and the other wall in contact with the oxides of the preceding claims.

19. A solid state oxygen sensor as claimed in any one of claims 1, 2 or 6 having one or both walls in contact with mixtures singles or complex of a material claimed in the preceding claims.

20. A solid state oxygen sensor for measuring partial pressures of oxygen substantially as hereinbefore described with reference to and as illustrated in the accompanying drawings.

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